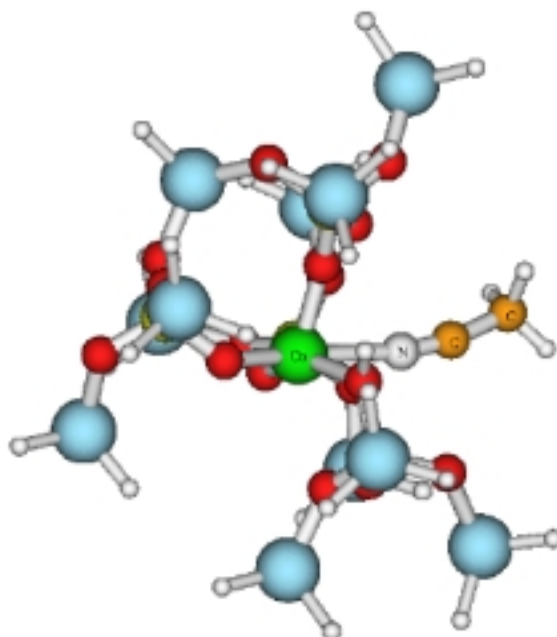


## Theoretical Studies of Catalysis of Transition Metals in Microporous Materials

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Zeolites are aluminosilicate-containing materials widely used in catalysis and separations applications because of the chemical selectivity provided by the molecular-sized pores. Transition metals can also be incorporated into the microporous structure to enhance the type of chemistry that can occur in these materials. Transition metal-substituted zeolites are used extensively to perform selective oxidation of chemical feedstocks. The transition metals can be located either at framework sites, where the metal has replaced a Si or other atom in the lattice, or at exchanged sites, where the metal has been exchanged for another cation on the interior surface of the material. For example, Ti framework sites in the zeolite TS-1 can perform selective oxidation of hydrocarbons using hydrogen peroxide. Similarly, Cu exchanged sites in the zeolite ZSM-5 have been actively studied in recent years to reduce nitrogen oxide emissions in automotive exhaust applications.

We have been applying a combination of theoretical approaches to model transition metal sites in microporous materials and to elucidate the fundamental interactions of molecules with these “active sites” in catalysis. Classical simulations employ a periodic approach to the lattice and treat the long-range electrostatic interactions that arise in these materials. Lattice energy minimization calculations give a reasonable description



**Figure 1:** Results of the structural minimization of acetonitrile ( $\text{CH}_3\text{CN}$ , at right) bound to a cluster model of CoAPO looking down the main channel.

**Transition metal-substituted zeolites are used extensively to perform selective oxidation of chemical feedstocks.**

of the geometric distortions near the transition metal site. These results can be incorporated in quantum chemical calculations employing cluster models to describe the interactions of molecular adsorbates with the transition metal and to treat bond-breaking and bond-formation processes that cannot be treated by the classical methods.

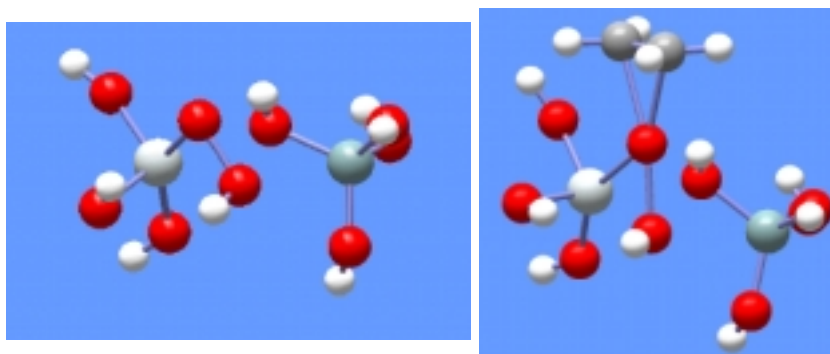
In a recent application we have examined the properties of Co ions in framework sites in the aluminophosphate ( $\text{AlPO}_4$ ) materials, which are close relatives of zeolites in the sense that they have Al-O-P instead of Al-O-Si linkages found in aluminosilicates. Using a combination of cluster calculations with lattice constraints from classical simulations, for example, we calculate the Co-O bond length to be 1.94 Å for Co(+2) in APO compared to 1.90 Å from EXAFS measurements on reduced cobalt in the material CoAPO-18. In Figure 1, we show the results of acetonitrile ( $\text{CH}_3\text{CN}$ ), an adsorbate that has been studied experimentally in CoAPO systems, bound to a Co(+2) framework site. The calculated Co-O (1.93 Å) and Co-N (2.08 Å) bond lengths agree well with values from EXAFS (1.93 Å and 2.05 Å, respectively) spectroscopic measurements.

These approaches have also been applied to Ti framework substitution for Si in the aluminosilicate zeolite ZSM-5 (denoted TS-1). The results of the bulk classical simulations show that the nearest

neighbor bond lengths to the nearest neighbor oxygen atoms typically increase by  $\sim 0.1$  Å compared to the original Si-O bond lengths. There are actually 12 crystallographically distinct sites where the Ti can be substituted. Our experimental colleagues at LANSCE (Los Alamos Neutron Science Center) and CST Division have refined the positions of Ti in TS-1 using neutron diffraction techniques. They have found that the Ti atoms are not randomly distributed among the 12 sites but preferentially are located at only three or four of the possible sites. The calculated substitution energies for Ti at these observed sites, however, do not show greater thermodynamical stability compared to the other sites. From these calculations and other theoretical analyses, we have concluded that kinetic factors in the synthesis of the zeolite using organic templates must account for the preferred locations of Ti substitution in TS-1.

Quantum chemistry calculations have examined fundamental reaction steps at the Ti site when TS-1 reacts with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and subsequently with

ethylene ( $\text{C}_2\text{H}_4$ ). In Figure 2 the results are shown for a relatively small cluster containing one Ti and one Si initially bridged by a Ti-O-Si linkage. In the calculations the outer atoms in the cluster are held fixed at the lattice positions found in the classical simulations. After the reaction with hydrogen peroxide, the Ti-O-Si bond is broken and is replaced by a Ti-OOH bond on one side and a Si-OH bond on the other. In the second step the ethylene attacks the Ti-OOH moiety and ultimately extracts the O atom to form ethylene oxide, leaving a Ti-OH bond. The first step is calculated to be slightly endothermic (+3 kcal/mol), while the second step is exothermic (-39 kcal/mol) with an activation barrier of +13 kcal/mol. In addition to probing the mechanisms of catalytic reactions in microporous materials, the calculated vibrational frequencies can assist in the interpretation of inelastic neutron scattering (INS) studies at LANSCE, where the low-energy vibrational modes of adsorbates such as  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and hydrocarbons in TS-1 can be probed.



**Figure 2:** (left panel) Result of addition of  $\text{H}_2\text{O}_2$  to the Ti-O-Si bond in TS-1 from cluster calculations [see text]. Atoms are colored as follows: O (red), H (white), Si (gray), ti (light gray at left) (right panel) Calculated transition state for the epoxidation of  $\text{C}_2\text{H}_4$  occurring at the Ti framework center in zeolite TS-1.